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## Aqueous Lanthanide Shift Reagents. 3. Interaction of the Ethylenediaminetetraacetate Chelates with Substituted Ammonium Cations

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**Abstract:** The ethylenediaminetetraacetate (EDTA) chelates of the trivalent lanthanides form in aqueous solution ion pairs with organic cations, e.g., substituted ammonium ions, and thereby can act as aqueous shift and relaxation reagents in these systems. By competition, the interaction of inorganic cations with  $\text{Ln}(\text{EDTA})^-$  can also be studied by  $^1\text{H}$  NMR. The pH profiles reveal that at pH values above 8 the hydroxo complex,  $\text{Ln}(\text{EDTA})(\text{OH})^{2-}$ , is formed, which also interacts with cations. The apparent dissociation constant of the  $\text{Pr}(\text{EDTA})^-(\text{CH}_3)_n\text{NH}_4^{n+}$  ion pair decreases with increasing methylation from 0.50 to 0.17 M (at 39 °C) and likewise the intrinsic induced shift decreases from 1.38 to 0.38 ppm. From these results, as well as from the relative broadenings induced by  $\text{Gd}(\text{EDTA})^-$ , it is concluded that in the ion pair one of the methyl groups is closer to the central lanthanide ion than the others. The mean distances between the methyl protons and the gadolinium were calculated from the intrinsic line widths. The values obtained for acetate, methylammonium, and tetramethylammonium are 5.3, 7.7, and 10.3 Å, respectively. The interaction with  $\text{Yb}(\text{EDTA})^-$  is very weak. This is in agreement with a previously suggested model for the structure of  $\text{Ln}(\text{EDTA})^-$  chelates in solution, which assumes that the lighter lanthanides are pentachelated and have a free acetate arm capable of interacting with cations. On the other hand, the heavier lanthanides are hexachelated and lack such an ability.

The suitability of the ethylenediaminetetraacetate (EDTA) chelates of the trivalent lanthanides as aqueous shift and relaxation reagents for carboxylate and chelating phenolate substrates has recently been established.<sup>1,2</sup> It might be intuitively anticipated that the  $\text{Ln}(\text{EDTA})^-$  chelates, by virtue of their negative charge, would interact with cations in solution. Indications for such interactions have been obtained from the effects of LiCl concentration upon the observed shifts in the acetate- $\text{Ln}(\text{EDTA})^-$  systems.<sup>1</sup> Presented in this article are the results of our studies on the interaction of substituted ammonium cations with  $\text{Pr}(\text{EDTA})^-$ , which is a shift reagent, and with  $\text{Gd}(\text{EDTA})^-$ , which is a relaxation reagent. Some experiments with the weakly interacting  $\text{Yb}(\text{EDTA})^-$  were also carried out. Details of the pH dependence of the induced shifts and line broadening, of the chemical equilibria, and of the structure of the complexes were elucidated. Additional evidence was obtained supporting our ideas<sup>1</sup> regarding the nature of the structural change of the EDTA chelates along the lanthanide series.

### Experimental Section

Solutions of the  $\text{Ln}(\text{EDTA})^-$  chelates were prepared and analyzed as previously described.<sup>1</sup> Analytical grade substituted ammonium chlorides of the free amines were used. The latter were employed in the study of the pH dependence. The highest pH investigated was attained by the addition of LiOD and the solution was then titrated with DCl. Reported pH values are meter readings corrected for deuterium isotope effects.

Proton NMR spectra were recorded on a Varian T-60 spectrometer operating at the ambient probe temperature of  $39 \pm 1$  °C. A small

amount of *tert*-butyl alcohol, ca. 0.1% v/v, served as an internal standard.

### Results

The effect of  $\text{Pr}(\text{EDTA})^-$  on the proton spectrum of the pyridinium cation is depicted in Figure 1. In contrast with the line overlap in the spectrum of pyridinium, the paramagnetic perturbation results in distinct and readily assignable multiplets. In particular  $\text{H}_2$  is shifted downfield by 0.3 ppm from its diamagnetic position.

Depending upon the relative concentrations of hydrogen or hydroxyl ions, either protonation<sup>3</sup> or formation of hydroxo complexes<sup>1</sup> of the  $\text{Ln}(\text{EDTA})^-$  chelates may occur. In addition, the ammonium cations, except for tetramethylammonium (TMA), undergo deprotonation at high pH. It is therefore imperative to investigate the pH profile of the induced shifts and line broadenings in this system. The pH profiles of the downfield shifts induced by  $\text{Pr}(\text{EDTA})^-$  in the proton resonances of methylammonium (MA) and TMA are shown in Figure 2. Also shown are the shifts in the absence of shift reagent. The shifts of MA are referred to the diamagnetic deprotonated base and those of TMA to its diamagnetic position. The induced shift for MA approaches zero at high pH indicating that methylamine interacts neither with  $\text{Pr}(\text{EDTA})^-$  nor with its hydroxo complex. On the other hand, for TMA a sign reversal of the induced shift is observed above pH 11. This indicates, as might be intuitively anticipated, that TMA interacts with  $\text{Pr}(\text{EDTA})(\text{OH})^{2-}$ . Referring to the dipolar shift relation

$$\delta_M = C(3 \cos^2 \theta - 1)/r^3 \quad (1)$$

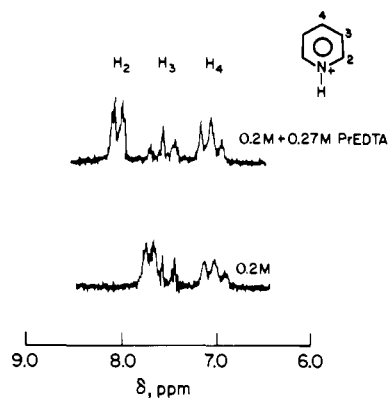
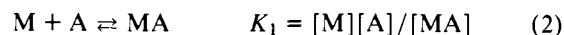


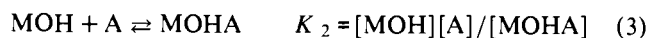
Figure 1. The 60-MHz  $^1\text{H}$  NMR spectra of the pyridinium cation in the absence (bottom) and in the presence (top) of  $\text{Pr}(\text{EDTA})^-$ .

it becomes clear that a sign reversal of the shift will occur if the angle  $\theta$  changes its value from  $\theta > 54^\circ 44'$  to  $\theta < 54^\circ 44'$ .

Further details regarding the interaction with the hydroxo complexes are revealed in the pH dependence of the  $\text{Gd}(\text{EDTA})^-$  induced line broadenings. These results are shown in Figure 3. Here a more dramatic difference in behavior between MA and TMA is observed. The line broadening of MA has a maximum at pH 10.1 and then rapidly decreases. For TMA a plateau between pH 10.5 and 11.5 is observed with further increase of the broadening with increasing the pH. The comparison shows that methylamine does not interact with  $\text{Gd}(\text{EDTA})^-$  or with its hydroxo complex. On the other hand, the MA and TMA cations associate with  $\text{Gd}(\text{EDTA})(\text{OH})^{2-}$ . All of the equilibria involving these species have to be considered in the analysis of the results. In addition, as indicated by Geier and Karlen,<sup>4</sup>  $\text{Gd}(\text{EDTA})^-$  is present as an equilibrium between two forms differing in one coordinated water molecule. Previous studies have shown that this equilibrium is affected by salt concentration.<sup>1</sup> In fact, high concentrations of  $\text{LiCl}$  were used in the experiments with the acetate- $\text{Gd}(\text{EDTA})^-$  in order to shift the equilibrium in one direction.<sup>1</sup> However, a similar approach is impractical with the present system because of the competition between  $\text{Li}^+$  and the substituted ammonium cations (vide infra). A detailed analysis of the pH profile was abandoned in view of the great complexity of the system. Rough estimates of the apparent dissociation constants and intrinsic line widths were obtained from measurements at constant pH. The line broadening,  $\Delta$ , at a constant  $\text{Gd}(\text{EDTA})^-$  concentration was measured as a function of the MA or TMA concentration. The relevant parameters were obtained from a plot of  $1/\Delta$  vs. the cation concentration.<sup>5</sup> Titrations were carried out below pH 8 and at about pH 10.5. At the lower pH only the equilibrium



was considered. Here M denotes the  $\text{Ln}(\text{EDTA})^-$  chelate, A the substituted ammonium ion, and MA the ion pair formed between the two. At the higher pH only the following equilibrium was assumed



where MOH is the hydroxo complex of  $\text{Ln}(\text{EDTA})^-$  and MOHA is its ion pair with the substituted ammonium cation. A summary of the parameters thus obtained is given in Table I. The intrinsic line widths should be compared with that of acetate in the acetate- $\text{Gd}(\text{EDTA})^-$  complex, which is 1620 Hz.<sup>1</sup> The line width due to the electron-nuclear dipolar interaction in paramagnetic complexes is given by the well-known Solomon equation<sup>6</sup>

$$1/T_{2M} = D r^{-6} f(\tau_c) \quad (4)$$

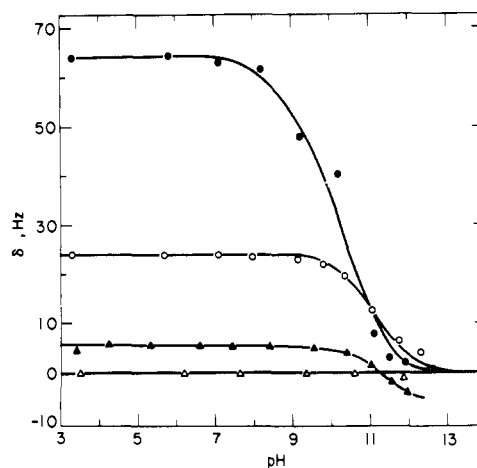


Figure 2. The pH dependence of the proton shifts of  $\text{CH}_3\text{NH}_3^+$  (circles) and of  $(\text{CH}_3)_4\text{N}^+$  (triangles) in the absence (open symbols) and in the presence (filled symbols) of  $\text{Pr}(\text{EDTA})^-$ . The shifts are relative to the corresponding high pH forms. Concentrations: 0.1 M  $\text{CH}_3\text{NH}_3^+$  with 0.35 M  $\text{Pr}(\text{EDTA})^-$ ; 0.04 M  $(\text{CH}_3)_4\text{N}^+$  with 0.1 M  $\text{Pr}(\text{EDTA})^-$ .

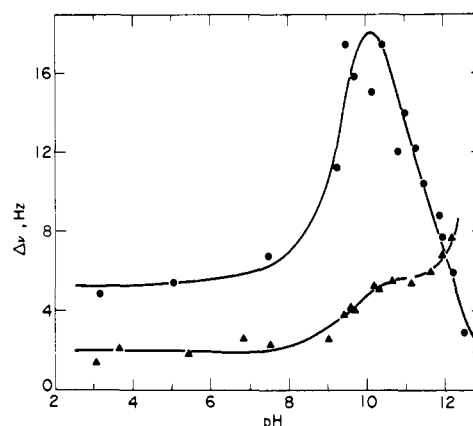
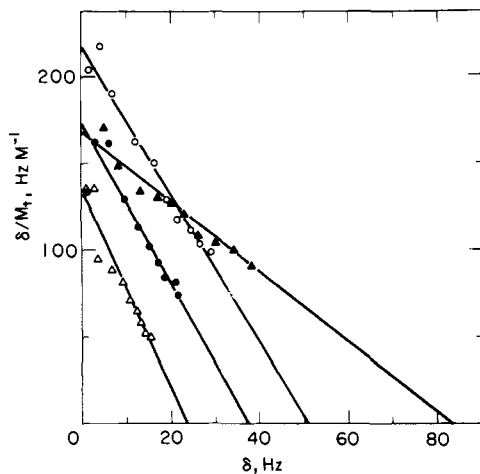


Figure 3. The pH dependence of the  $\text{Gd}(\text{EDTA})^-$ -induced line broadenings of  $\text{CH}_3\text{NH}_3^+$  (circles) and  $(\text{CH}_3)_4\text{N}^+$  (triangles). Concentrations: 0.051 M  $\text{CH}_3\text{NH}_3^+$  with 0.012 M  $\text{Gd}(\text{EDTA})^-$ ; 0.03 M  $(\text{CH}_3)_4\text{N}^+$  with 0.009 M  $\text{Gd}(\text{EDTA})^-$ .

Table I. Intrinsic Induced Shifts and Apparent Dissociation Constants of  $\text{Pr}(\text{EDTA})^--(\text{CH}_3)_n\text{NH}_{4-n}^+$  Ion Pairs

	$\delta_1$ , Hz	$K_1$ , M
$\text{CH}_3\text{NH}_3^+$	83	0.50
$(\text{CH}_3)_2\text{NH}_2^+$	51	0.24
$(\text{CH}_3)_3\text{NH}^+$	37	0.21
$(\text{CH}_3)_4\text{N}^+$	23	0.17

where  $f(\tau_c)$  is a function of the correlation time and  $D$  is a known constant. Note that owing to the inverse sixth power dependence upon the distance between the central ion and the nucleus of interest distances calculated from relaxation data are rather insensitive to the inaccuracies in determining the values of  $1/T_{2M}$  and  $f(\tau_c)$ . With the reasonable assumption of  $\tau_c = 7 \times 10^{-11}$  s for the correlation time,<sup>7</sup> the distance between the acetate protons and Gd was calculated and found to be 5.3 Å. The corresponding values for MA and TMA are 7.7 and 10.3 Å, respectively. While the absolute values are subject to some reservations, the relative distances are free of many of the assumptions involved. Clearly the acetate protons are much closer to the central ion than those of the substituted ammonium cations.



**Figure 4.** Plots of  $\delta/[M_1]$  vs.  $\delta$ , where  $[M_1]$  is the total concentration of  $\text{Pr}(\text{EDTA})^-$  and  $\delta$  is the downfield shift of the  $(\text{CH}_3)_n\text{NH}_{4-n}^+$  cations relative to their unperturbed state, at  $\text{pH} < 8$ . Concentrations and symbols:  $\text{CH}_3\text{NH}_3^+$  0.023 M, filled triangles;  $(\text{CH}_3)_2\text{NH}_2^+$  0.030 M, open circles;  $(\text{CH}_3)_3\text{NH}^+$  0.026 M, filled circles;  $(\text{CH}_3)_3\text{NH}^+$  0.026 M, filled circles;  $(\text{CH}_3)_4\text{N}^+$  0.037 M, open triangles.

**Table II.** Intrinsic Line Widths and Apparent Dissociation Constants of  $\text{Gd}(\text{EDTA})^--(\text{CH}_3)_n\text{NH}_{4-n}^+$  Ion Pairs

	$\text{CH}_3\text{NH}_3^+$	$(\text{CH}_3)_4\text{N}^+$
$\Delta_1,^a$ Hz	180	30
$K_1,^a$ M	0.25	0.06
$\Delta_2,^b$ Hz	900	108
$K_2,^b$ M	0.51	0.13

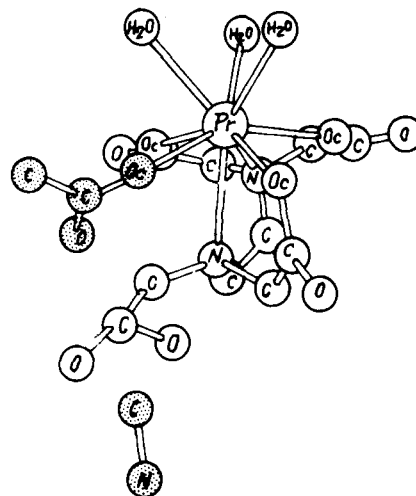
<sup>a</sup> pH 7-8. <sup>b</sup> pH 10-11.

The interaction of  $\text{Pr}(\text{EDTA})^-$  with the series of cations of the type  $(\text{CH}_3)_n\text{NH}_{4-n}^+$ , where  $n = 1, 2, 3$ , or 4, was studied at the constant pH of 7.0. Relatively high reagent concentrations were employed to titrate a constant concentration of  $(\text{CH}_3)_n\text{NH}_{4-n}\text{Cl}$ . Under such conditions  $[M_f] \cong [M_1]$  and the following equation applies<sup>1</sup>

$$\delta/[M_1] = \delta_1/K_1 - \delta/K_1 \quad (5)$$

Thus the data are amenable to graphical analysis. The results are presented in Figure 4. Fairly good linear relationships are obtained. The values of the intrinsic induced shift  $\delta_1$  and the apparent dissociation constant  $K_1$  are summarized in Table II. It is seen that ion-pair formation is favored by increasing methylation while the intrinsic shift decreases. A similar trend is observed with the corresponding parameters of  $\text{Gd}(\text{EDTA})^-$  (cf. Table I). The interaction of methylethylammonium with  $\text{Pr}(\text{EDTA})^-$  was investigated in a similar manner. The intrinsic induced shifts thus obtained are 77 Hz for the  $\alpha$ -methyl protons and 65 and 53 Hz respectively for the methylene and methyl protons of the ethyl moiety. An attempt to study the interaction of MA with  $\text{Yb}(\text{EDTA})^-$ , which is an upfield shift reagent, showed that the association in this system was rather weak. Only order of magnitude estimates of the relevant quantities could be obtained. They are  $\delta_1 = -180$  Hz and  $K_1 = 3.3$  M.

The interaction of  $\text{Pr}(\text{EDTA})^-$  with a number of other cations was studied in a qualitative manner by competition with TMA. The effect of 0.25 M  $\text{Pr}(\text{EDTA})^-$  on the TMA shift in 1:1 mixtures of TMA and other salts (1 M each) was measured and compared to the shift obtained when only TMA was present. From the shift differences, the following order of increasing tendency for ion pairing was obtained:  $\text{Cs}^+ < \text{Rb}^+ < \text{NH}_4^+ < \text{Li}^+ < \text{TMA}$ . Another series of experiments using MA resulted in the order:  $\text{Cs}^+ < \text{Rb}^+ < \text{NH}_4^+ < \text{Li}^+ < \text{MA}$



**Figure 5.** A schematic model of the solution structure of  $\text{Pr}(\text{EDTA})^-$  showing the possible sites of interaction with acetate and methylammonium ions. Hydrogen atoms omitted for clarity. Adapted from the x ray scale model of  $\text{La}(\text{EDTA})^-$ .<sup>9</sup>

$< \text{Pr}^{3+}$ . Note that the competitive effect of the paramagnetic  $\text{Pr}^{3+}$  could also be investigated.

## Discussion

The capacity of paramagnetic  $\text{Ln}(\text{EDTA})^-$  chelates to serve as shift or relaxation reagents for organic cations in aqueous solution has been demonstrated. This or appropriately chosen analogous systems could serve as models for studying anion-cation interactions in aqueous solutions by NMR. The limitations often imposed by the lack of nuclei that are suitable for NMR experiments can be overcome by observing a proton-containing cation and studying the competitive effect of other cations, which may be either diamagnetic or paramagnetic. With the series of methylammonium cations,  $(\text{CH}_3)_n\text{NH}_{4-n}^+$ , clear trends are observed both in their tendency to associate with  $\text{Pr}(\text{EDTA})^-$  and in their intrinsic induced shifts. The apparent dissociation constants increase and the shifts decrease with progressive methylation. It has recently been proposed on the basis of  $^{13}\text{C}$  NMR data for a series of  $\epsilon$ - $N$ -methyllysines that the charge density on the  $\epsilon$ -carbon atoms decreases with progressive methylation, thereby increasing the affinity for anionic species.<sup>8</sup> Our results may serve as an additional proof of this point. The variation of induced shifts along the series of cations, the relative induced shifts in the methylethylammonium cation, as well as the  $\text{Gd}(\text{EDTA})^-$  induced relative broadenings for MA and TMA all point toward the possibility that a methyl group is situated close to the central lanthanide ion and is probably intimately involved in ion pairing.

It has previously been suggested that there are two forms of EDTA chelates along the lanthanide series.<sup>1</sup> With the lighter lanthanides, e.g., praseodymium, the central ion is pentachelated by the ligand thus permitting the coordination of an additional carboxylate. In this form one of the acetate arms of EDTA is free and it is plausible that it is the site for cation association. A possible arrangement of ligands is shown in Figure 5, for which the scale model of Hoard et al.<sup>9</sup> has appropriately been modified. With the heavier lanthanides, e.g., ytterbium, the central ion seems to be hexachelated by the EDTA ligand thus lacking the ability to coordinate an additional acetate or to associate with a cation. The finding that  $\text{Yb}(\text{EDTA})^-$  hardly interacts with MA is in accord with this model. While only a rough estimate of the intrinsic induced shift in the latter system could be obtained, we note that its ratio with that induced by  $\text{Pr}(\text{EDTA})^-$  is  $-2.2$  in agreement

with the theoretical predictions for dipolar shifts in axially symmetric isostructural complexes of ytterbium and praseodymium.<sup>10</sup>

The formation of hydroxo complexes of the Ln(EDTA)<sup>-</sup> chelates, previously inferred from the effect of pH on the induced shifts and broadenings of acetate, is confirmed by the pH profiles in the present work. Here, however, the cations associate with Ln(EDTA)(OH)<sup>2-</sup> and larger broadenings induced by gadolinium are observed as pH > 8. The complications in the data interpretation that may arise from the presence of multiple equilibria can be avoided by working at pH < 8.

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## Aqueous Lanthanide Shift Reagents. 4. Interaction of Pr<sup>3+</sup>, Nd<sup>3+</sup>, and Eu<sup>3+</sup> with Xylitol. Origin of Induced Shifts in Polyols

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**Abstract:** Xylitol interacts in aqueous solution with trivalent lanthanides to form 1:1 as well as 2:1 complexes. The apparent dissociation constants, evaluated from an analysis of the lanthanide-induced shifts, show that the stability of the complexes increases in the sequence Pr < Nd < Eu. Details on the method of data analysis and on the criteria for assessing the reliability of the resulting parameters are given. An interpretation of the induced shifts in this and related systems indicates that nuclei close to the site of lanthanide complexation experience large contact shifts.

The recent interest in studying the complexes between metal ions and carbohydrates is related to their possible involvement in a number of biological processes.<sup>1,2</sup> Angyal has shown that proton NMR methods can be applied to the study of such complexes in aqueous solution.<sup>3</sup> In particular it has been demonstrated that paramagnetic lanthanides induce appreciable shifts in the spectra of some aldoses,<sup>4</sup> alditols,<sup>5</sup> and cyclitols.<sup>6,7</sup> Lanthanides have been used to afford spectral resolution in a study of the interaction of xylitol with xylose isomerase<sup>8</sup> and to induce stereospecific relaxation rate enhancements in a number of mono- and disaccharides<sup>9</sup> and aldohexuronic acids.<sup>10</sup> Lanthanide-induced shifts in the spectra of methyl- $\alpha$ -D-gulopyranoside<sup>11</sup> and methyl- $\alpha$ -D-galactopyranosiduronate<sup>12</sup> have been treated as being of a purely dipolar origin and used to determine the structure of the complexes. However, results obtained for *epi*-inositol with a number of lanthanides indicate the presence of large contact contributions to the induced shifts.<sup>6,7</sup> The utilization of lanthanide-induced shifts for structure elucidation requires not only the evaluation of the dipolar shift contribution, but also the determination of the stoichiometry of the complex, in view of possible complications due to higher than 1:1 complexes. Predominantly 1:1 sugar-cation complexes are formed with D-lyxose, D-ribose,<sup>13</sup> and methyl- $\alpha$ -D-gulopyranoside.<sup>11</sup> In the *cis*-inositol-calcium system a 2:1 complex has been detected in addition to the prevalent 1:1 complex.<sup>14</sup> While 1:1 stoichiometry has tacitly been assumed for alditols,<sup>5,15</sup> the formation of 2:1 complexes cannot be ruled out.

In an attempt to answer some of the questions regarding the stoichiometry of alditol-lanthanide complexes and the origin

of their proton shifts, we have investigated the interaction of xylitol with Pr<sup>3+</sup>, Nd<sup>3+</sup>, and Eu<sup>3+</sup>. The lanthanide-induced shifts were monitored in two types of titrations, in which the concentration of one of the components is held constant and that of the other varied. The two sets of data thus obtained are compatible only if 2:1 complexes are included in the analysis. An interpretation of lanthanide-induced shifts in this and related systems is also presented.

### Experimental Section

Lanthanide chlorides, rather than the nitrates used by other workers,<sup>5,15</sup> were employed throughout this work.<sup>16</sup> Their solutions were prepared from the corresponding oxides (Research Chemicals, Phoenix, Ariz.) by treatment with analytical grade hydrochloric acid. Concentrations were determined by EDTA titrations using Arsenazo as the end-point indicator. Xylitol was obtained from Sigma Chemical Co., St. Louis, Mo., and used without further purification. Solutions were made up in D<sub>2</sub>O containing ca. 0.1% v/v *tert*-butyl alcohol, which served as an internal reference for the chemical shift measurements. Proton NMR spectra were recorded on a Varian T-60 spectrometer at the ambient probe temperature of 39 ± 1 °C.

### Results

At 60 MHz the proton spectrum of xylitol consists of a featureless band centered at 2.45 ppm from *tert*-butyl alcohol. The effects of successive additions of EuCl<sub>3</sub> are depicted in Figure 1. Already at low concentrations a well resolved and readily assignable spectrum is obtained. As seen in Figure 1, complex formation markedly alters the coupling constant  $J_{2,3}$  from 4.5 Hz at the lowest EuCl<sub>3</sub> concentration to <2 Hz at the highest.